THE MECHANISM OF IRON ATOM PRODUCTION IN THE MULTIPHOTON DISSOCIATION OF ORGANOMETALLIC IRON COMPLEXES

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An examination of the reaction pathway in the 2+1 multiphoton dissociation of a series of related iron tricarbonyl organometallic complexes is reported. The study includes the use of pressure-dependent measurements and the application of RRKM theory to explore the reaction mechanism. It is concluded on the basis of the relative intensities of the observed iron electronic transition and the statistical calculations, that ground-state molecular fragments are produced via a statistical, stepwise pathway and that the Fe final product states result from further direct excitation to a dissociative channel. This conclusion contrasts with recent studies of $Cr(CO)_6$ which indicate that two different mechanisms are active, leading to different product quantum states.

1. Introduction

Multiphoton excitation of organometallic complexes has been known for some time to result almost exclusively in the production of bare metal atoms [1]. Recently, interest has centered on the mechanism of this dissociation process in both iron and chromium complexes [2–10]. More specifically, Hepburn and co-workers [5] have shown that the UV multiphoton dissociation of $Fe(CO)_5$ is best described as a series of successive RRKM events, each of which results in the loss of a single carbonyl fragment. This mechanism is proposed even though the absorption of the first (193 nm) photon is sufficient to effect dissociation of three carbonyl groups. A similar conclusion was reached by Vernon and coworkers [10] based on a moment analysis of their molecular beam data. On the other hand, the dissociation of ferrocene is believed to proceed via a direct process by which the complex is coherently excited to a dissociative potential energy surface and surface crossings result in the observed distribution of Fe product states [2,3]. In the case of chromium hexacarbonyl, a recent report [9] invokes both of the mechanisms noted above in order to rationalize the multitude of observed product states.

Recently, we reported the results of a 2+1 MPD experiment involving a series of structurally related iron tricarbonyl organometallic complexes [4]. The general structure of these complexes may be noted as $Fe(CO)_3L$, with $L=C_4H_6$, C_6H_8, C_8H_8 and three isomers of C_8F_8. In these experiments, 2+1 REMPI was used as a detection scheme for the analysis of the Fe electronic levels produced in the MPD process. The only detected signals were due to neutral iron atoms and relative populations of the three lowest electronic states were reported. The object of the experiment was to discern the relative influence of ligand vibrational modes and Fe–ligand bond energy in the distribution of excited metal atom states resulting from the dissociation of the initially prepared excited states of the complexes. Although no definitive statement could be made with regard to the reaction pathway, two characteristics of this pathway were inferred from the results:

(1) the relative populations of the excited states were controlled by the availability of ligand vibrational modes for energy redistribution and;

(2) given equivalent or nearly equivalent densities of vibrational states, the controlling factor was the bond dissociation energy.

In light of the recent studies from the laboratories cited above, we have re-examined some of the members of the same series of iron complexes used in the original study, concentrating on the butadiene (BUT) and octafluorocyclooctatetraene (OFCOT)

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complexes as representative, but including measurements at a range of added background gas pressures. In addition, an extensive series of RRKM calculations have been performed. Based upon the literature cited above, at least three plausible mechanisms may be constructed for the MPD of the target molecules. These mechanisms are:

(a) "explosive" decomposition in which the $Fe(CO)_3L$ complex is excited well beyond the total bond enthalpy and all of the bonds are broken simultaneously by a statistical process;

(b) direct photodissociation of the complex by excitation to a repulsive potential energy surface and;

(c) a sequential loss of ligands commensurate with the available energy. In this scheme, bonds are broken as soon as a particular energy threshold is reached.

In addition, due to the large number of molecular bonds and the high levels of excitation, some combination of these "pure" mechanisms rather than any one of mechanisms (a)–(c) may be consistent with the observed data. *The goal of this research is to use the data in our earlier report in conjunction the experimental results reported here and with statistical calculations to identify the mechanism appropriate for the MPD of the $Fe(CO)_xL$ series of organometallic complexes.* We show in this report that both the ground-state multiplet and the excited-state intensities are dependent upon the total gas pressure. Moreover, the results are consistent with statistical dissociation of the three carbonyl groups after excitation of the organometallic complex to the two-photon level with the final metal atom product states resulting from direct excitation of the remaining fragment to a dissociative potential surface. Curve crossings with this potential surface control the distribution of other product states.

2. Experimental

The output of an excimer-pumped dye laser (Lumonics T861-S/EPD-330) passed through a 15 cm focal length quartz lens into an ionization cell containing the sample vapor. The experimental cell was of the now standard parallel plate design [11] having a spacing of 2.5 cm with an applied potential of −300 V. Careful experimentation indicated that at this potential (and at potentials up to the limit of the power supply, 600 V) the apparatus was operated in the ionization chamber rather than the proportional counter regime, i.e. no amplification was observed and the total ion signal was independent of the voltage. Laser pulse energies were of the order of 1 mJ over a duration of approximately 15 ns. Greater pulse energies resulted in power broadened atomic spectra. All measurements were made with 0.02 Torr of organometallic sample vapor, but the total pressure varied between 0.02 and 50 Torr by use of added Ar or N_2. Spectra were obtained over the single photon wavelength range from 445 to 451 nm and recorded in steps of 0.005 nm by means of a gated integrator (Stanford Research Systems) and a laboratory microcomputer. Special care was taken to ensure that all measurements were made under identical conditions of applied field, laser focusing and laser polarization (linear). All samples were obtained from Strem Chemical and used without further purification. Argon and nitrogen were Research Grade and purchased from Airco.

Since the cell was operated in the ionization chamber mode, the added background gas had no effect on the observed signal except to lower the ion mobility and increase the transit time to the electrode [12]. Therefore, any changes in the observed current could be attributed to photophysical/photochemical processes. In order to account for this increase in transit time, the ionization signal was observed on a transient recorder and the gated integrator delay and width were adjusted so that the same fraction of the total current pulse (4%) was included in the gated period at all pressures. This direct method of adjusting the integration parameters is preferred to attempts to infer corrections from theoretical expressions for the variation in arrival time with molecular density.

3. Results and discussion

The energy level diagram for $Fe(CO)_3C_4H_6$ is shown in fig. 1. It may be seen that the available energy from the initial two-photon step is sufficient to dissociate all three carbonyl fragments. In our earlier research [4], it was qualitatively shown that the dissociation mechanism of all of the complexes was

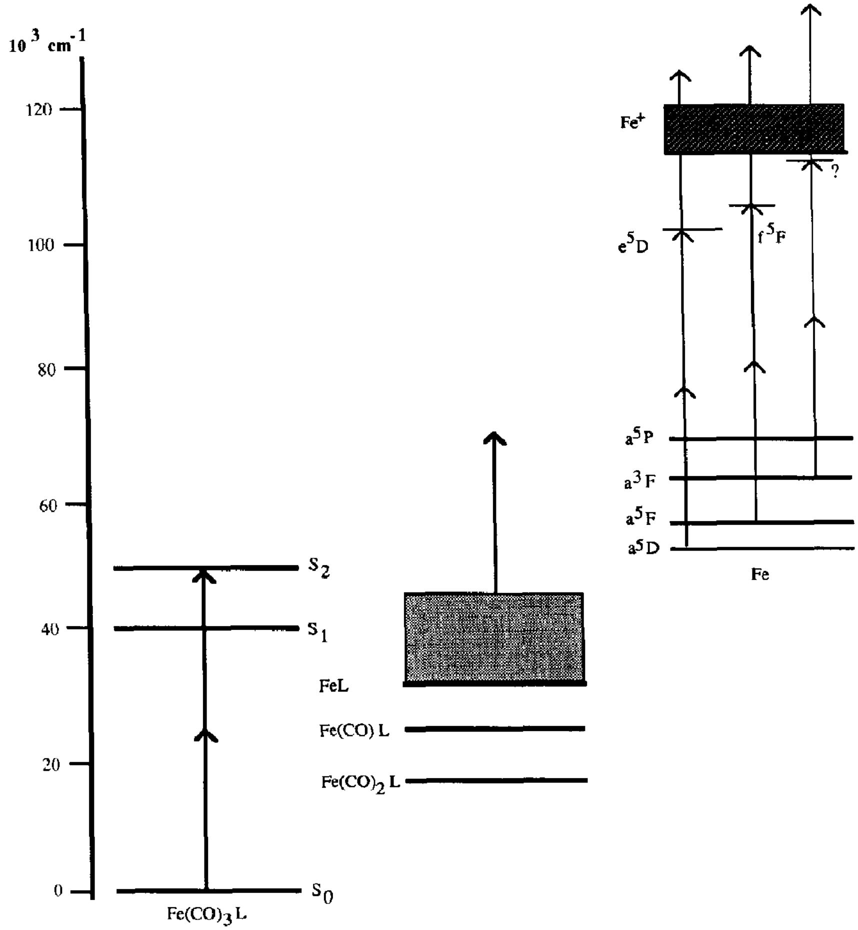

Fig. 1. Energy level diagram for the Fe(CO)$_3$L molecules. The particular energetics shown correspond to L = C_4H_6. The diagram is drawn to scale with the total bond enthalpy of Fe(CO)$_3$$C_4H_6$ taken from ref. [13]. Using an average Fe–CO bond strength of 1.22 eV, as is employed in refs. [13,14], the energies of the unsaturated fragments are estimated to be the values shown in the figure. The atomic energy levels are those of Moore [15]. Arrows represent a photon of wavelength 447 nm.

similar and the actual product distribution was strongly dependent on the density of vibrational modes of the ligand. A more quantitative example of this behavior is shown in fig. 2, where the correlation between the ^3F relative populations reported in the earlier work [4] and the vibrational density of states at a total excitation energy of 8.25 eV for the organic ligand is clear. (The method used for counting the density of states is described below.) It is also necessary to note that, although absolute intensities were not reported in our earlier study, under a given set of conditions the signal strength of all of the transitions decreased with increasing complexity of the ligand. The smallest signals in the original study [4] were obtained for the C_8F_8 complexes. The implication is that the rate of formation of product decreases with increasing complexity of the ligand. We, therefore, concluded that the initial step involved release of the carbonyl groups and that the subsequent single photon absorption led to dissociation of the Fe–L bond. The longer association of the organic ligand with the Fe atom resulted in increased proba-

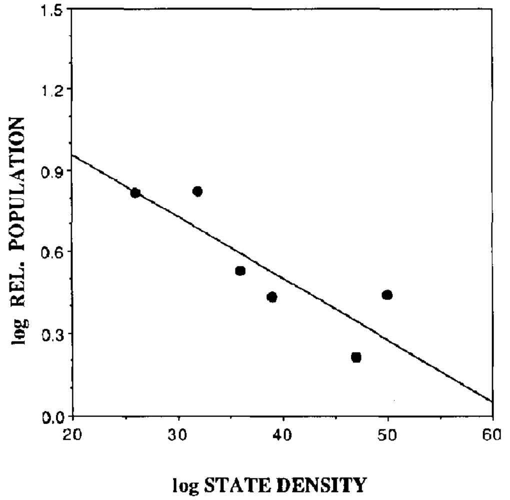

Fig. 2. Log–log plot of the dependence of the relative excited ^3F state Fe populations on the available density of states (per cm^{-1}) of the organic ligand at a total energy of 8.25 eV. The density of states function was calculated via the Beyer–Swinehart algorithm and the populations were reported in ref. [4]. The solid line is a linear least squares fit through the experimental points.

bility of energy redistribution to the ligand modes and, hence, the sensitive dependence of the excited state population on the mode density. The preferential breaking of Fe–CO bonds is consistent with observations in gas phase organometallic substitution reactions [16,17]. Returning to fig. 1, it is clear that the absorption of the third photon is sufficient to result in complete molecular dissociation and that the iron atoms so produced may be detected as an ion current by means of 2+1 REMPI. Moreover, at these laser wavelengths, 445–451 nm, the total energy absorbed by the molecule is sufficient to produce iron atoms in the lowest three electronic levels.

The effect of collisions on the MPD process was studied by recording the change in ion current with increasing buffer gas pressure. The intensity of the current signal was observed to be a strongly decreasing function of the pressure. Therefore, the absolute experimental uncertainties were greatest at the highest pressures used in this study. We estimate, from repetitive experiments, that the average uncertainty is 10%. The signals due to the individual members of the ground-state multiplet, as well as the ^3F product states were obtained. In general, the effect of added N_2 was greater than that of Ar, but the magnitude of the effect was independent of the nature of the complex. The two complexes chosen for this study represent the extremes of the original set with respect to the available density of states. Within experimental error, the relative populations of the members of the ground-state multiplet (i.e. the Boltzmann temperature) and the population of the excited-state iron product relative to the ground state, were unchanged by the addition of the buffer gases.

Welch et al. [18] have employed an exponential model to describe pressure-dependent rate constants for collisional energy transfer in organometallic systems,

$$k=c_1 \exp(-c_2 P) . \qquad (1)$$

We have applied the same model to our data, of which a typical example, the $Fe(CO)_3C_4H_6$ complex with added nitrogen and argon, is shown in fig. 3. Data such as this have been fit to eq. (1) (the solid line in the figure) to determine the effect of the buffer gas and the results for the coefficients c_1 and c_2 are collected in table 1. As noted, Ar is only about one-half as efficient as nitrogen in reducing the current arising from the atomic products detected by MPI,

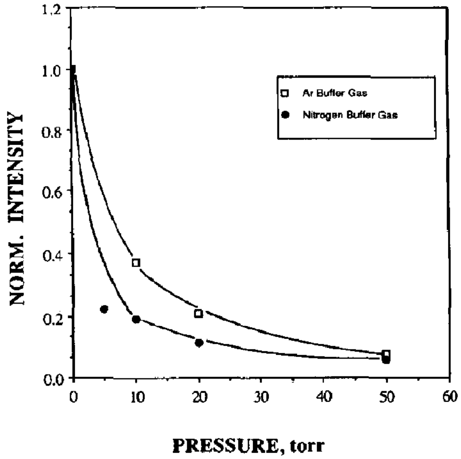

Fig. 3. Normalized ion current for the MPI transition originating at the $^5D_4$ level of atomic iron and resulting from MPD of $Fe(CO)_3C_4H_6$. The lines drawn through the experimental data points represent the fit to the data by eq. (1) using the parameters of table 1.

Table 1
Pressure effects in the measured Fe MPI current resulting from MPD of $Fe(CO)_3L$ (experimental coefficients [a] for eq. (1))

Molecule	Background gas	Fe level	c_1 (s^{-1})	c_2 ($Torr^{-1}$)
butadiene	nitrogen	a $^5D_4$	0.987	0.135
		a $^5D_3$	0.835	0.130
		a $^5D_2$	0.791	0.115
		a $^5D_1$	0.891	0.098
		a $^5D_0$	0.734	0.092
		a ^3F_J	0.908	0.107
	argon	a $^5D_4$	0.994	0.067
		a $^5D_3$	0.999	0.084
		a $^5D_2$	0.986	0.057
		a $^5D_1$	0.987	0.059
		a $^5D_0$	0.882	0.063
		a ^3F_J	0.884	0.044
OFCOT	nitrogen	a $^5D_4$	1.002	0.118
		a $^5D_3$	0.999	0.186
		a $^5D_2$	1.001	0.122
		a $^5D_1$	1.004	0.204
		a $^5D_0$	1.001	0.110
		a ^3F_J	0.981	0.136
	argon	a $^5D_4$	0.999	0.051
		a $^5D_3$	0.990	0.073
		a $^5D_2$	0.998	0.062
		a $^5D_1$	0.987	0.057
		a ^3F_J	0.910	0.052

[a] The average uncertainties (1σ) in the coefficients are ± 10% for c_1 and ± 20% for c_2.

but for a given buffer gas the magnitude of the relaxation is identical for both the ground and excited states. The fact that an atomic collision partner has the same effect as a molecular buffer gas is indicative of a collisional energy transfer process involving an internally excited, molecular intermediate. The redistribution of the initial excitation energy into vibrational modes means the amount of energy transferred to the buffer gas is relatively small in comparison to the electronic to translational energy transfer necessary in collisional processes involving the atomic resonant intermediates in the MPI detection scheme [19]. Moreover, the observation of an identical energy transfer process for both the ground and excited states of the products is an indication that the two channels have a common intermediate. If atomic collisional relaxation were the correct mechanism, one would expect that the relaxation of the ^3F_J state would be twice as efficient as that of the ground state [19].

A series of RRKM calculations were performed for the entire series of complexes using the Beyer–Swinehart counting algorithm for computing the density of vibrational levels. In these calculations, we attempted to ascertain whether or not the mechanism of iron production is consistent with various statistical mechanisms or a series of statistical processes. Table 2 shows the results of an RRKM calculation in which three photons are assumed to be absorbed, followed by "explosive" decomposition of the complex to produce ground state Fe, i.e. mechanism (a) of section 1. The rate constants resulting from that calculation are much too small to allow for the observation of any product during the time scale of the experiment, which is the laser pulse width of ≈ 15 ns. We have also performed a calculation based on a series of three sequential statistical decays after the absorption of two quanta of energy, with subsequent absorption of a third photon by the remaining FeL fragment, resulting in statistical decomposition of

Table 2
RRKM calculations for direct three-photon formation of ground state Fe atoms ("explosive" formation)

Ligand	Excess energy (eV)	k (s^{-1})
C_4H_6	2.47	1.5×10^{-2}
C_6H_8	2.57	1.3×10^{-4}
C_8H_8	2.67	2.3×10^{-5}
C_8F_8 (η^4)	2.17	1.1×10^{-10}
C_8F_8 (η^3+σ bond)	0.77	1.9×10^{-22}
C_8F_8 (η^2)	2.37	5.0×10^{-11}

Table 3
RRKM calculations for formation of FeL and Fe by the sequential mechanism

Ligand	$k_{2h\nu}$ (s^{-1}) ($Fe(CO)_3L \rightarrow FeL+3CO$)	$k_{3h\nu}$ (s^{-1}) ($FeL \rightarrow Fe+L$)
C_4H_6	3.2×10^{9}	2.6×10^{7}
C_6H_8	2.8×10^{9}	2.2×10^{6}
C_8H_8	5.6×10^{8}	7.5×10^{5}
C_8F_8 (η^4)	1.1×10^{8}	1.2×10^{2}
C_8F_8 (η^3+σ bond)	1.1×10^{8}	1.7×10^{-8}
C_8F_8 (η^2)	4.0×10^{7}	1.0×10^{2}

that fragment as well. The sequential process was suggested by Hepburn and co-workers [5] and Vernon and co-workers [10] for the MPD mechanism of $Fe(CO)_5$ and sequential loss of CO ligands from the pentacarbonyl has been directly observed by Weitz and co-workers [20]. The results of the calculations are shown in table 3 and yield rate constants for FeL production within the range which could ultimately produce a quantity of iron atoms easily detected in the MPI detection scheme employed. The trend in rate constant is also in agreement with the trend observed in signal intensity in ref. [4], i.e. signal intensity is proportional to the redistribution rate constant. However, table 3 also indicates that statistical decay of the FeL fragment upon absorption of a third photon is only realistic within the time frame of the experiment in the case of the smallest ligands and earlier work [4] has shown that the mechanism for all of the complexes is identical. Therefore, we must also eliminate mechanism (c) from consideration.

The RRKM calculation has ruled out a statistical production of all fragments, leaving mechanism (b), direct photodissociation, as the only alternative of the "pure" mechanisms. The production of triplet atomic products is inconsistent with a direct transition to a dissociative potential surface leading to the observed photofragments. The latter would be forbidden by symmetry correlation rules. It is hypothetically possible that the initial excitation does lead to a very highly excited singlet surface, followed by intersystem crossing and subsequent decomposition of the complex along a triplet surface, but the pressure and density of vibrational states dependences of the MPD process make such a mechanism unlikely. This analysis eliminates mechanism (b) from consideration and we must now consider a mechanism which is a synthesis of the options outlined in section 1. We believe that the following pathway is consistent with all of the data and inherently reasonable. Earlier research [20] has shown that the initial excitation of the parent pentacarbonyl at these energies is a singlet–singlet transition, but that rapid intersystem crossing occurs. In particular, for the complexes currently under study, extrapolation of this analysis implies that the RRKM decomposition to the FeL fragment occurs along a triplet potential surface which correlates with the ground states of all of the unsaturated fragments. To continue with the proposed mechanism, the FeL triplet fragment so formed absorbs an additional photon to populate an excited, dissociative state which directly correlates with the ^3F iron–singlet organic ligand products. In this model, the ground state is populated by curve crossings of the potential surface which leads to ^5D iron atoms with the directly prepared triplet surface of FeL. Further support of the proposed mechanism arises from the relative populations of the ^3F atoms reported in our earlier work [4]. If one assumes that the transitions are saturated and that the reported relative populations in our earlier research [4] are approximately the true populations, in all instances, the excited state is overpopulated in comparison to the temperatures extracted from the ground-state populations. Even in the absence of saturation, based on typical Einstein coefficients and the fact that both of the REMPI atomic transitions employed in this study are strongly allowed, the excited state must still be overpopulated in comparison to the statistical temperatures of the ground-state multiplet. The most reasonable rationale for such a distribution is the statistical decomposition–direct excitation scheme proposed above. Moreover, the similarity of the ground-state multiplet distribution regardless of the organic ligand is readily reconciled to this mechanism. In retrospect, the proposed mechanism is a synthesis of those proposed for iron pentacarbonyl [5], mechanism (c), and ferrocene [2,3], mechanism (b). Such behavior is entirely reasonable since the complexes employed in the study are, indeed, intermediate between these two extremes of carbonyl substitution.

4. Conclusions

By means of pressure-dependent MPI intensity measurements and statistical calculations, it has been shown that organometallic complexes of the general formula $Fe(CO)_3L$ undergo visible wavelength multiphoton dissociation via a mechanism which involves both rapid energy redistribution and direct excitation. Both the ground and excited electronic state products were shown to evolve according to the same mechanism. In this reaction pathway, the complex is initially excited via two-photon absorption to the S_2 excited state, but undergoes rapid intersystem crossing to a triplet potential surface. The -CO ligands are sequential expelled along this surface, which correlates with the ground electronic states of the sequential fragments. The absorption of the third photon by the remaining FeL fragment populates an excited triplet state, which evolves directly to the ^3F Fe product state. The ^5D ground state is populated by a curve crossing with this directly prepared FeL excited state, leading to similar effective ground state Boltzmann temperatures regardless of the nature of the organic ligand. Although the 2+1 MPD process has not been applied to any other organic-substituted iron carbonyl complexes, the proposed mechanism is sufficiently general as to be applicable to any member of the general class of $Fe(CO)_xL$ molecules.

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